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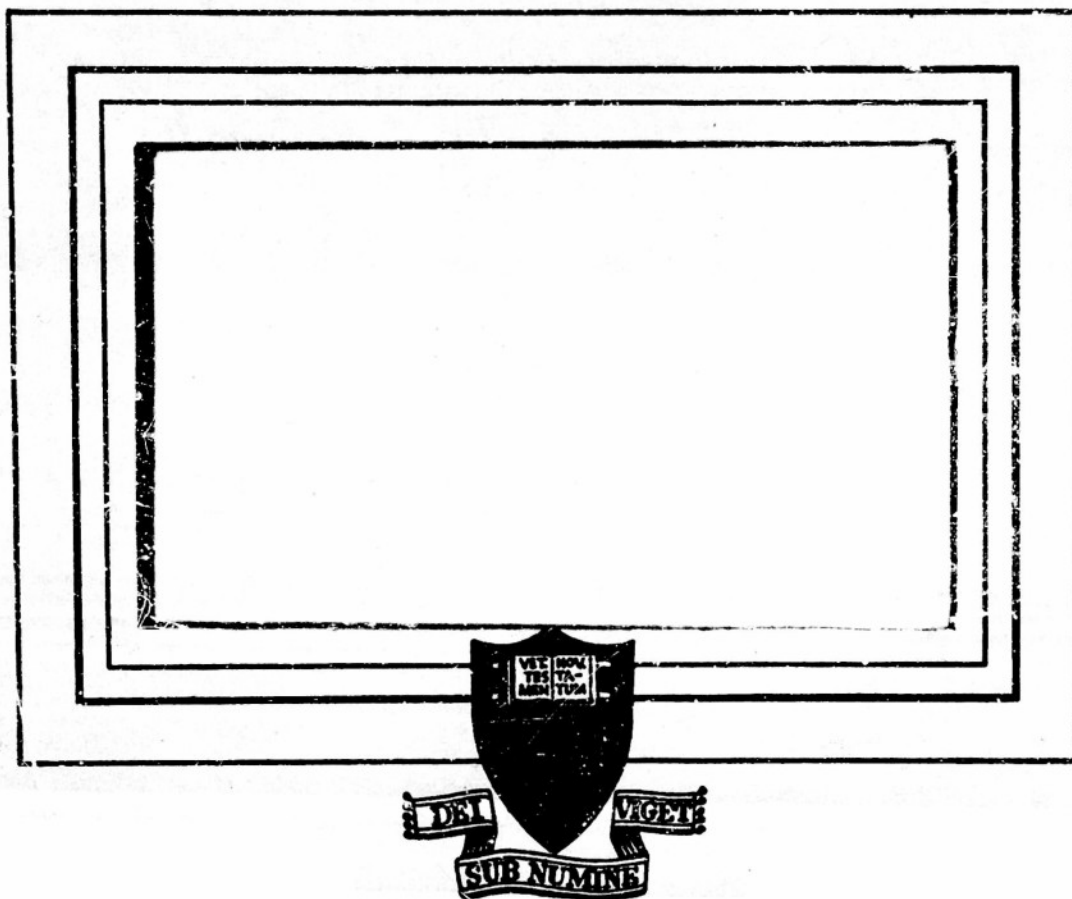
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PRINCETON UNIVERSITY

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Contract N6-ori-105, Task Order IV

Dielectric Properties and the Structure
of Matter

Charles P. Smyth, Project Leader

Report No. 31

Periodic Status Report

January 1 - March 31
1953

Department of Chemistry

Princeton University

U.S. Navy Department

Office of Naval Research

Washington, D.C.

Dielectric Properties and the Structure of Matter

Periodic Status Report, January 1 - March 31, 1953

Charles P. Smyth

Previously reported measurements by Mr. R.S. Holland of the dielectric constant and loss at microwave frequencies have been used to obtain a critical wavelength of 0.66 cm. for methyl chloroform in dilute solution in carbon tetrachloride at 20°. This value and the low value 0.07 found for the empirical distribution coefficient of the relaxation times are practically indistinguishable from the values previously observed in this laboratory for *t*-butyl chloride, which has a molecule very similar in size and shape. Similar measurements on solutions of pyridine in heptane at a wavelength of 1.24 cm. have been combined with measurements by Dr. G.N. Roberts at 6.6, 10 and 30 cm. to obtain critical wavelengths of 0.45 cm. at 1°, 0.42 cm. at 20° and 0.36 cm. at 40° with very small values of the distribution coefficient.

The apparatus for the investigation of crystalline solids at 3.2 cm. wavelength is still undergoing alteration and adjustment by Mr. D.E. Williams.

In collaboration with the research program of the Project, Dr. G.N. Roberts, Mr. A. DiGiacomo and Mr. A. Tulinskie have carried out further dielectric investigations. Dr. Roberts has extended the range of an apparatus previously constructed for use at 23 to 30 cm. wavelength so that measurements of dielectric constant and loss have been made with it, as mentioned above, down to 6.6 cm., and may probably be made up to 60 cm. wavelength. Dr. Roberts has also used a low-frequency bridge to measure the dielectric constants and losses of mixtures of polar liquids cooled to a glassy state. The results show that mixtures of an associated and a non-associated liquid give two maxima in the curve for loss against temperature, while a mixture of two non-associated liquids gives rise to only one maximum. Further measurements will involve the dilution of such binary mixtures with a viscous, non-polar solvent.

The dipole moment of hexamethyldisiloxane has been investigated because of the similarity of some of its bonds to those in the very important silicones. Mr. DiGiacomo has measured the dielectric constant of the vapor over a range of temperature and pressure. The lack of variation of the polarization with temperature indicates zero moment for the molecule, the large atomic polarization observed for the vapor being sufficient to account for the apparent moment value reported in the literature on the basis of solution measurements. However, Mr. Holland has found an appreciable loss at 1.24 cm. for this substance in the liquid state, which indicates polarity in the molecule. The increase in the loss with decreasing temperature indicates that the critical wavelength, at which the loss is a maximum, is much shorter than 1.24 cm. and much shorter than would be expected for a polar molecule of this size. The very interesting possibilities of this problem will be further investigated when a new sample of the substance has been obtained.

In addition to hexamethyldisiloxane, the following seven substances have been measured in the vapor state, the dipole moments of the first five having been measured by Mr. DiGiacomo and those of the last two by Mr. Tulinskie.

Dipole Moments ($\times 10^{18}$)	
Difluorodibromomethane	0.66
Trifluoromethane	1.62
Trifluorochloromethane	0.46
Trifluorobromomethane	0.65
Trifluoroiodomethane	0.92
Pentafluoroethane	1.54
Perfluorodimethyl ether	0.54

These moment values are being used to study mutual inductive effects within the molecules.

Scientific Papers July 1 - March 31, 1953

"Microwave Absorption and Dielectric Relaxation in Some Long-Chain Esters." by P.L. McGeer, A.J. Curtis, G.B. Rathmann and C.P. Smyth. Presented before the American Physical Society, Denver, Col., July 1, 1952.

"Microwave Absorption and Molecular Structure in Liquids. VIII, Dielectric Relaxation in Some Long-Chain Esters," by P.L. McGeer, A.J. Curtis, G.B. Rathmann and C.P. Smyth, Journal of the American Chemical Society, 74, 3541 (1952).

"Microwave Absorption and Molecular Structure in Liquids. IX. Measurement in Organic Halides at 10 cm. Wavelength," by F.H. Branin, Jr. and C.P. Smyth. Journal of Chemical Physics, 20, 1121 (1952).

"A Calculation of the Static Dielectric Constant of Ice," by J.G. Powles, Journal of Chemical Physics, 20, 1302 (1952).

"Dielectric Relaxation in d-Camphor," by J. G. Powles, Journal of Chemical Physics, 20, 1648 (1952).

"The Dipole Moments and Molecular Structures of Cycloheptatrienone and Three Tetracyclones," by Armand DiGiacomo and Charles P. Smyth, Journal of the American Chemical Society, 74, 4411 (1952).

"The Determination of Complex Dielectric Constants of Absorptive Liquids by Microwave Interferometry," by Franklin H. Branin, Jr., Journal of Applied Physics, 23, 990 (1952).

"Dielectric Dispersion in the Microwave Region of Six Tetrasubstituted Methanes in the Solid State," by J.G. Powles, D.E. Williams and C.P. Smyth, Journal of Chemical Physics, 21, 136 (1953).

"The Dipole Moments and Structures of cis- and trans-1,2-Dichlorocyclohexane," by A. Tulinskie, A. DiGiacomo and C.P. Smyth.

Sent to Journal of the American Chemical Society.

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